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(54) **Modified Phillips catalysts for  
olefin polymerisation**

(57) A catalyst for polymerising 1-  
olefins comprises (1) a heat activated  
catalyst base comprising chromium  
oxide and nickel oxide supported on a  
refractory oxide and (2) an  
organometallic compound. The olefin

is preferably ethylene or a mixture of  
ethylene with other 1-olefin(s). The  
refractory oxide can be silica or  
alumina for example, and the  
organometallic compound is  
preferably a magnesium, boron or  
aluminium alkyl. The polymerisation  
medium optionally contains a polyene  
modifier, e.g. butadiene.

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## SPECIFICATION

## Polymerisation process

The present invention relates to a process for polymerising 1-olefins and to a catalyst suitable for use therein.

More particularly the invention relates to a process for polymerising 1-olefins, for example ethylene, using a modified Phillips catalyst. Phillips catalysts have been extensively described in the literature. They are formed by supporting chromium trioxide, or a compound calcinable thereto, on a refractory oxide support material, for example silica, alumina, zirconia, thoria or silica-alumina and heating in a non-reducing atmosphere, preferably an oxidising atmosphere to produce an active polymerisation catalyst. The produced catalyst is used to polymerise 1-olefins using the so-called "solution form" or "particle form" process. In the "solution form" process the monomeric 1-olefin which is normally ethylene or a mixture of ethylene with up to about 40 wt% of other 1-olefins, is contacted with a suspension of the catalyst in a liquid hydrocarbon which is solvent for the polymer at the polymerisation temperature employed. In the "particle form" process the monomer 1-olefin is contacted with a suspension or a fluidised bed of the catalyst particles in a fluid medium under conditions such that the polymeric 1-olefin forms as solid particles suspended in or fluidised in the fluid medium. The fluid medium can be for example a liquid hydrocarbon or a gas. Examples of suitable liquid hydrocarbons are isobutane and n-pentane. Examples of suitable gases are nitrogen or argon mixed with the gaseous monomer, or the undiluted gaseous monomer. Processes of this type are described in, for example UK Patent Specifications 790,195, 704,641, 853,414, 886,784 and 899,156.

United States Patent 2,969,348 discloses a Phillips catalyst comprising chromium oxide and an oxide of nickel associated with a carrier, for example silica-alumina, wherein at least some and preferably at least 0.1% by weight of the chromium (based on the weight of the catalyst composite) is in the hexavalent state.

The present invention provides a process for polymerising monomer comprising ethylene or a mixture of ethylene with up to 40 wt% (based on total monomer) of other 1-olefinic monomer comprising (a) forming a catalyst base comprising one or more refractory oxide support materials having supported thereon a chromium compound which is chromium oxide or a compound calcinable thereto and a nickel compound which is nickel oxide or a compound calcinable thereto, (b) heating the catalyst base under such conditions that an active polymerisation catalyst is formed, (c) contacting the monomer with the active polymerisation catalyst in the presence of one or more organometallic compounds having the general formula  $MR^2_pY_{q-p}$  wherein M is boron or a metal of groups 1A, 2A, 2B or 3A of the Periodic Table (Mendeleef),  $R^2$  is an alkyl, cycloalkyl or aryl group containing 1 to 10 carbon atoms, Y is hydrogen, halogen or alkoxide, q is the valency of M and p is an integer from 1 to q. For the purposes of the present invention organo-boron compounds are regarded as organometallic although boron is not strictly a metal.

In a preferred embodiment according to the present invention step (c) is carried out in the presence of a polyene modifier.

The monomer employed in the present invention is either ethylene or a mixture of ethylene with up to 40 wt%, preferably up to 25 wt% of other 1-olefinic monomer; 1-butene, 1-pentene, 1-hexene or 4-methyl-1-pentene are preferred.

The chromium compound supported on the catalyst base can be chromium oxide (i.e.  $CrO_3$ ) or a compound calcinable thereto, for example chromium nitrate, chromium carbonate, chromium acetate, ammonium chromate, chromyl chloride or tertiary butyl chromate.

The nickel compound supported on the catalyst base can be nickel oxide or a compound calcinable thereto, for example nickel nitrate, nickel acetate, nickel chloride, nickel sulphate or organic complexes of nickel.

The one or more refractory oxide support materials can be, for example silica, silica-alumina, silica-titania, alumina, zirconia or thoria. Silica is preferred, particularly silica having a mean particle diameter in the range 20 to 150 microns; and a surface area in the range 150 to 600 square metres per gramme.

The quantity of chromium compound supported on the refractory oxide is suitable such as to provide a chromium concentration of at least 0.1%, preferably in the range 0.2—30 wt%, most preferably 0.3 to 5.0 wt% based on the total weight of catalyst base.

The quantity of nickel compound supported on the refractory oxide support material is suitably such as to provide a nickel concentration of at least 0.1%, preferably in the range 0.5 to 10%, based on the total weight of catalyst base.

The chromium compound and the nickel compound can be supported on the one or more refractory oxide support materials separately or together. For example the nickel compound can be supported on a first refractory oxide support material and the chromium compound on a second refractory oxide support material which can be the same as or different from the first support material, and then the two support materials bearing the supported compounds are combined to produce the catalyst base. Or, for example, the nickel compound and the chromium compound can be added as a mixture or successively to the support material.

The supporting of the chromium compound on the refractory oxide support material can be

achieved, for example, by dissolving a soluble chromium compound in a volatile liquid, impregnating the support material with the solution and evaporating the solvent; by impregnating the support with a liquid chromium compound, e.g. chromyl chloride; by passing the vapour of a volatile chromium compound, e.g. chromyl chloride, into a bed of the support material; or by mixing together a finely divided chromium compound and the support material in the presence of a small quantity of solvent, the quantity being insufficient to cause substantial agglomeration of the support material, continuing the mixing until a substantially homogeneous mix is obtained and then evaporating the solvent. Examples of solutions that can be used to impregnate the support material are chromium trioxide/water, ammonium chromate/water, chromium acetate/water, tertiary butyl chromate/hexane, chromyl chloride/chloroform.

The nickel compound can be supported on the support material using similar techniques to those employed in the supporting of the chromium compound. Preferably the support material is impregnated with an aqueous or non-aqueous solution of a soluble nickel compound and then the solvent is evaporated; examples of suitable impregnating solutions that can be employed are nickel nitrate/water, nickel acetate/water, nickel chloride/alcohol and nickel dimethyl glyoxime derivative/alcohol.

For further techniques of forming catalyst bases comprising chromium compounds and nickel compounds supported on refractory support material, reference may be made to US Patent 2,969,348.

After the desired quantity of chromium compound and nickel compound have been supported on the support material, the catalyst base is heated under conditions such that the chromium compound and the nickel compound are retained as or are converted to chromium oxide and nickel oxide respectively and such that an active polymerisation catalyst is formed, by which is meant that the active polymerisation catalyst must be capable of polymerising ethylene.

The temperature to which the catalyst base must be heated to form an active polymerisation catalyst (hereinafter referred to as the activation temperature) is at least 250°C and not higher than the temperature at which the support commences to sinter. Preferably the activation temperature is in the range 400 to 900°C, most preferably 500 to 800°C. In general, the higher the activation temperature employed within the aforementioned ranges, the lower becomes the average molecular weight of polyolefin produced over the catalyst. The heating time is suitably within the range 5 minutes to 24 hours, preferably 30 minutes to 15 hours although times outside the broader range can be employed if desired.

It was formerly believed that to be an effective polymerisation catalyst a "Phillips" catalyst must contain at least some chromium in hexavalent form. Whilst it is true that most, if not all, "Phillips" catalysts do contain hexavalent chromium it is now believed that the olefin polymerisation catalysis may operate through chromium in valency states below 6. Nevertheless it is desirable during the heat activation of catalysts of this type, including the catalyst employed in the process of the present invention, that conditions which favour the formation of, or retention of, chromium in the higher valency states should be employed. The heat activation is preferably carried out in a non-reducing atmosphere and most preferably in an oxidising atmosphere or in vacuo. Dry air is an example of a suitable oxidising atmosphere. The heat activation must be performed under anhydrous or dehydrating conditions and the activated catalyst must be protected from ingress of moisture.

The metal present in the organometallic compound in the present invention is preferably magnesium, boron or aluminium. Organometallic compounds particularly preferred are triethyl aluminium, triisobutyl aluminium, triethyl boron or dibutyl magnesium. The quantity of organometallic compound employed is suitably 0.5 to 50%, preferably 1 to 20% based on the total weight of catalyst.

The polymerisation conditions employed in the present invention can be any of the conditions used in Phillips polymerisation processes. Preferably the polymerisation conditions are the so called "particle form" process conditions. In the "particle form" process the monomeric 1-olefin is contacted with a suspension or a fluidised bed of the catalyst particles in a fluid medium under conditions such that the polymeric 1-olefin forms as solid particles suspended in or fluidised in the fluid medium.

The fluid medium employed in particle form process conditions can be a liquid or a gas. Preferably it is a liquid. Examples of suitable liquid media are hydrocarbons which are chemically inert and non-deleterious to the modified catalyst under the reaction conditions. Preferred liquid media are paraffins or cycloparaffins having from 3—30 carbon atoms per molecule, for example isopentane, isobutane, cyclohexane. Most preferably the liquid medium is isobutane.

When a liquid medium is employed in the process of the present invention preferably the concentration of monomer therein is in the range 2—10 wt% although concentrations outside this range can be employed if desired.

When the process of the present invention is under particle form process conditions the polymerisation temperature is preferably in the range 50 to 112°C, most preferably 80 to 108°C.

The polymerisation pressure is preferably in the range 2 to 100 bar when the fluid medium is a liquid and 1 to 60 bar when the fluid medium is a gas. The residence or reaction time can vary from a few minutes to several hours and is generally in the range 15 minutes to 3 hours. The particle form process can be conducted under batch or continuous polymerisation conditions. Preferably the conditions are continuous. Preferred apparatus for conducting the reaction under continuous conditions in a liquid medium is described in UK Patent Specification 899,156.

For further details of examples of solution form and particle form process conditions and apparatus

which can suitably be employed in the present invention, reference may be made to UK Patent Specification Nos: 790,195, 804,641, 899,156, 886,784 and 853,414.

In the preferred embodiment of the present invention wherein step (c) is carried out in the presence of a polyene modifier, the polyene is suitably a C<sub>4</sub> to C<sub>20</sub> polyene, the polyene may be substituted by alkyl, cycloalkyl, or aryl groups or may be unsubstituted. Preferably the polyene contains 2 double bonds. Examples of suitable polyenes are butadiene, isoprene, 1,5-hexadiene, 1,4-hexadiene, myrcene, cyclopentadiene, dicyclopentadiene and ethylidene norbornene. The quantity of polyene employed is suitably 0—50 parts by weight, preferably 0 to 10 parts by weight per unit weight of catalyst.

The polyene can be introduced into the step (c) in any desired manner, for example by feeding into the polymerisation reactor by itself or together with the catalyst monomer or diluent.

Isolation of the produced polymer may be conducted using the techniques well known in the art. Any residual organometallic compound in the produced polymer can, if desired, be deactivated, for example, by treating the polymer with a suitable reagent, for example water, steam, moist inert gas or alcohol.

The present invention further provides a catalyst for polymerising 1-olefins prepared by (a) forming a catalyst base comprising one or more refractory oxide support materials having supported thereon a chromium compound which is chromium oxide or a compound calcinable thereto, and a nickel compound which is nickel oxide or a compound calcinable thereto, (b) heating the catalyst base under such conditions that an active polymerisation catalyst is formed, and (c) adding to the active polymerisation catalyst one or more organometallic compounds having the general formula  $MR^2_pY_{q-p}$  wherein M is boron or a metal of groups 1A, 2A, 2B or 3A of the Periodic Table (Mendeleef), R<sup>2</sup> is an alkyl, cycloalkyl or aryl group containing 1 to 10 carbon atoms, Y is hydrogen, halogen or alkoxide, q is the valency of M and p is an integer from 1 to q.

The catalyst of the present invention is preferably prepared using the components and preparation conditions herein described.

The invention is illustrated in the following Examples.

#### EXAMPLE 1

##### (a) Catalyst Preparation

Nickel acetate tetrahydrate [3.2 g, Ni(O<sub>2</sub>CCH<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O] was dissolved in water (30 ml). This was then added to 30 g of a commercial chromia on silica (ID969, W. R. Grace and Co). The produced catalyst base was then dried at 150°C in a vacuum oven. The catalyst base was activated by heating at 700°C for 5 hours in a bed fluidised with 900 ml/min of dry air. After cooling, the catalyst was stored under dry nitrogen. Analysis showed that it contained 1.04% by weight Cr, 2.6% by weight Ni and 0.62% by weight Cr<sup>VI</sup>.

##### (b) Polymerisation

Polymerisation was carried out in a 2.3 litre stainless steel stirred autoclave. The reactor was purged with nitrogen, baked out for 2 hours at 110°C, then cooled to 105°C. 457 mg of the catalyst prepared as described above was charged to the reactor followed by a mixture of 0.20 ml of a 10% by weight solution of triethyl aluminium in n-hexane (=17 mg triethyl aluminium) in 1 litre of dry isobutane.

The reactor temperature was maintained at 105°C and ethylene was added to bring the total pressure in the reactor to 41.4 bar. Ethylene was added continuously throughout the run to maintain this pressure. Polymerisation and polymer property data are shown in Table 1.

#### EXAMPLE 2

##### (a) Catalyst Preparation

Catalyst Preparation was as in Example 1 except that the final catalyst contain 1.0% by weight Cr, 3.1% by weight Ni and 0.68% by weight Cr.

##### (b) Polymerisation

Polymerisation was carried out in a 2.3 litre stainless steel stirred autoclave. The reactor was purged with nitrogen, baked out for 2 hours at 110°C, then cooled to 100°C. 417 mg of the catalyst prepared as described above was charged to the reactor followed by a three component mixture comprised of 1.7 mg triethylaluminium, 2.1 g 1,3-butadiene and 1 litre of dry isobutane.

The reactor temperature was maintained at 100°C and ethylene was added to bring the total pressure in the reactor to 41.4 bar. Ethylene was added continuously throughout the run to maintain this pressure. Polymerisation and polymer property data are shown in Table 1.

**EXAMPLE 3****(a) *Catalyst Preparation***

The catalyst used in Example 2 was also used in Examl. 3.

**(b) *Polymerisation***

- 5 The polymerisation was carried out as described in Example 2 except that the polymerisation was carried out at 104°C and the weight of butadiene used was 2.2 g. Polymerisation and polymer data are shown in Table 1. 5

TABLE 1  
Polymerisation and Polymer Property Data :  
Nickel, alkyl and diene-modified Phillips catalyst system

Example	Butadiene wt (g)	wt % Nickel in Catalyst	Catalyst wt (g)	Polymerisation			Polymer				
				Time (min)	Temp (°C)	Yield (g)	MI <sub>2,16</sub> <sup>1</sup>	MI <sub>21,6</sub> <sup>2</sup>	MIR	Kd <sup>3</sup>	Density <sup>4</sup> (kg.m <sup>-3</sup> )
1	0	2.6	0.475	39	105	415	0.19	9.8	51	2.5	943
2	2.1	3.1	0.417	44	100	188	0.02	5.6	234	9.6	954
3	2.2	3.1	0.417	43	104	355	0.09	10.1	105.1	6.3	952

Notes:

- 1) Determined according to BS2783, method 105°C.
- 2) Determined by a method similar to that described in ASTM D1238, procedure A, condition F.
- 3) Determined by a method similar to that given in Sabia, R. J. Appl. Poly. Sci. 1963, 7, 347.
- 4) Determined by a method similar to that given in BS 2782, Part 5, 1965, Method 509B.

## CLAIMS

1. A process for polymerising monomer comprising ethylene of a mixture of ethylene with up to 40 wt% (based on total monomer) of other 1-olefinic monomer comprising (a) forming a catalyst base comprising one or more refractory oxide support materials having supported thereon a chromium compound which is chromium oxide or a compound calcinable thereto, and a nickel compound which is nickel oxide or a compound calcinable thereto, (b) heating the catalyst base under such conditions that an active polymerisation catalyst is formed, (c) contacting the monomer with the active polymerisation catalyst in the presence of one or more organometallic compounds having the general formula  $MR^2_pY_{q-p}$  wherein M is boron or a metal of groups 1A, 2A, 2B or 3A of the Periodic Table (Mendeleef),  $R^2$  is an alkyl, cycloalkyl or aryl group containing 1 to 10 carbon atoms, Y is hydrogen, halogen or alkoxide, q is the valency of M and p is an integer from 1 to q. 5
2. A process as claimed in claim 1 wherein step (c) is carried out in the presence of a polyene modifier. 10
3. A process as claimed in claim 1 to 2 wherein ethylene is the sole 1-olefinic monomer. 15
4. A process as claimed in claim 1 or 2 wherein up to 25 wt% of other 1-olefinic monomer is present, (based on total monomer). 15
5. A process as claimed in any one of the preceding claims wherein the chromium compound is chromium oxide, chromium nitrate, chromium carbonate, chromium acetate, ammonium chromate, chromyl chloride or tertiary butyl chromate. 20
6. A process as claimed in any one of the preceding claims wherein the nickel compound is nickel oxide, nickel nitrate, nickel acetate, nickel chloride, nickel sulphate or an organic complex of nickel. 20
7. A process as claimed in any one of the preceding claims wherein the refractory oxide support material comprises silica. 25
8. A process as claimed in any one of the preceding claims wherein the quantity of chromium compound supported on the refractory oxide is such as to provide a chromium concentration in the range 0.2 to 30 wt% based on the total weight of catalyst base. 25
9. A process as claimed in any one of the preceding claims wherein the quantity of nickel compound supported on the refractory oxide support material is such as to provide a nickel concentration in the range 0.5 to 10% based on the total weight of catalyst base. 30
10. A process as claimed in any one of the preceding claims wherein the heat activation is carried out at a temperature in the range 400—900°C. 30
11. A process as claimed in any one of the preceding claims wherein the heat activation is carried out at a temperature in the range 500—800°C. 35
12. A process as claimed in any one of the preceding claims wherein the metal in the organometallic compound is magnesium, boron or aluminium. 35
13. A process as claimed in any one of the preceding claims wherein the organometallic compound is triethyl aluminium, triisobutyl aluminium, triethyl boron or dibutyl magnesium. 40
14. A process as claimed in any one of the preceding claims wherein the quantity of organometallic compound employed is 0.5 to 50% based on the total weight of catalyst. 40
15. A process as claimed in any one of the preceding claims wherein the polymerisation conditions are particle form process conditions as herein defined. 40
16. A process as claimed in claim 15 wherein the polymerisation fluid medium is a liquid hydrocarbon. 45
17. A process as claimed in claim 16 wherein the liquid hydrocarbon is isopentane or isobutane. 45
18. A process as claimed in any one of claims 15—17 wherein the polymerisation temperature is in the range 50—112°C. 45
19. A process as claimed in claim 2 wherein the polyene modifier is butadiene, isoprene, 1,5-hexadiene, 1,4-hexadiene, myrcene, cyclopentadiene, dicyclopentadiene or ethylidene norbornene. 50
20. A process as claimed in any one of the preceding claims wherein the quantity of polyene modifier employed is in the range 0—50 parts by weight per unit weight of catalyst. 50
21. A process substantially as hereinbefore described in any one of the Examples. 50
22. Polyethylene or ethylene copolymers prepared by the process claimed in any one of the preceding claims. 55
23. A catalyst for polymerising 1-olefins prepared by (a) forming a catalyst base comprising one or more refractory oxide support materials having supported thereon a chromium compound which is chromium oxide or a compound calcinable thereto, and a nickel compound which is nickel oxide or a compound calcinable thereto, (b) heating the catalyst base under such conditions that an active polymerisation catalyst is formed, and adding to the active polymerisation catalyst one or more organometallic compounds having the general formula  $MR^2_pY_{q-p}$  wherein M is boron or a metal of groups 1A, 2A, 2B or 3A of the Periodic Table (Mendeleef),  $R^2$  is an alkyl, cycloalkyl, halogen or alkoxide, q is the valency of M and p is an integer from 1 to q. 60